2001 Architectural Coatings Survey

Draft Reactivity Analysis

November 2003

California Environmental Protection Agency

Air Resources Board

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

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Acknowledgements

The Air Resources Board would like to thank the companies that responded to our 2001 Architectural Coatings Survey.

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ARB, Board	Air Resources Board
ASTM	American Society for Testing and Materials
CAS#	Chemical Abstract Service number
CMIR	Composite Maximum Incremental Reactivity
MIR	Maximum Incremental Reactivity
MIRBC	Maximum Incremental Reactivity of the Base Case ROG Mixture
NOx	Nitrogen Oxides
O$_3$	Ozone
PWMIR	Product Weighted Maximum Incremental Reactivity
RAF	Reactivity Adjustment Factor
RAVOC	Reactivity-Adjusted Volatile Organic Compound Content
ROG	Reactive Organic Gases
RR	Relative Reactivity
RRAC	Reactivity Research Advisory Committee
TOG	Total Organic Gases
TPD	Tons Per Day
U.S. EPA	United States Environmental Protection Agency
SCAQMD	South Coast Air Quality Management District
SCM	Suggested Control Measure
SWA	Sales-Weighted Average
SWAMIR	Sales-Weighted Average Maximum Incremental Reactivity
SWAMIR$_{VOC}$	Sales-Weighted Average Maximum Incremental Reactivity, based on VOCs only
U.S. EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound

Chapter 1 -- **Introduction and Background**

In July 2001, the Air Resources Board (ARB or Board) conducted a survey of companies that sold architectural coating products in California in 2000. This report contains a detailed analysis of the photochemical reactivity associated with architectural coatings, based on results from that survey.

When coatings are applied, they release different types of organic compounds that can react in the atmosphere to produce different amounts of ozone. This ozone forming potential is called hydrocarbon reactivity and it is determined by the photochemical reactions in the atmosphere. If a coating contains a small amount of a highly reactive compound, it could have a relatively high reactivity rating even if it has a low level of volatile organic compounds (VOCs). Similarly, a coating that has a high VOC content may have a relatively low reactivity rating, if it contains compounds that aren't very reactive.

2001 Architectural Coating Survey

ARB's 2001 Architectural Coating Survey gathered detailed sales information and speciation of VOCs in product formulations, with ingredients reported to the 0.1 weight percent level. Results from this survey are summarized in the "2001 Architectural Coatings Survey, Final Report, October 2003".

Suggested Control Measure

Architectural coatings are a large source of VOC emissions. In 2000, architectural coatings emitted approximately 128 tons per day of VOCs in California, on an annual average basis. To reduce emissions from this source, the Board approved a Suggested Control Measure for Architectural Coatings (SCM) in June 2000. As of October 2003, 18 local air districts have adopted the architectural coating limits from the SCM.

During the June 2000 Board hearing, Board members adopted Resolution 00-23 which directed the ARB staff to work with industry and other stakeholders in assessing the ozone-forming potential (i.e., reactivity) of architectural coatings, and to evaluate the feasibility of developing a reactivity-based control strategy. This evaluation is to include:

(1) assessing the reactivity of individual VOC species in consideration of the best available science;
(2) conducting a comprehensive survey of the architectural coatings industry; and
(3) assessing the extent to which VOCs emitted from architectural coatings contribute to ozone levels.

Testimony at the June 2000 hearing underscored industry's interest in reactivity-based limits and suggested that improved science is a prerequisite to developing reactivity-based limits.

In June 2001 and December 2002, ARB staff provided updates to the Board, regarding progress in implementing Resolution 00-23.[1] A brief summary of ARB's progress is provided below:

(1) ARB has funded a $300,000 research project with the University of California, Riverside that includes conducting chamber experiments to verify the chemical mechanisms used to identify the maximum incremental reactivities for some key solvents in architectural coatings. These solvents include Texanol® and several hydrocarbon solvents.

(2) In 2001, ARB conducted a comprehensive survey of the architectural coatings industry. Results from this survey are summarized in the "2001 Architectural Coatings Survey, Final Report, October 2003".

(3) ARB is using the data from the 2001 survey to estimate the reactivity of architectural coatings. The preliminary results are summarized in Chapter 2 of this report.

Reactivity-Based Regulations

The ARB has pioneered the use of reactivity in regulations controlling VOC emissions. In 1991, the Board approved the Low Emission Vehicles and Clean Fuels regulation that allowed for the use of reactivity adjustment factors.[2] In June 2000, the Board approved a reactivity-based regulation for aerosol coatings.[3]

Advantages of a Reactivity-Based SCM for Architectural Coatings

Many of the elements of a successful reactivity program are met with architectural coatings. Architectural coatings are a discrete and well-defined emissions source category. The reactivities of many VOC ingredients used in architectural coatings are already well characterized. Several manufacturers have expressed interest in working with us on a reactivity-based SCM.

There are several incentives to develop a reactivity-based control strategy. Mass-based emission reductions are becoming more difficult because architectural coatings are already more than 80 percent water-borne. Thus, reactivity-based limits offer a new opportunity to achieve additional ozone reductions. We expect an equal or greater air quality benefit compared to a mass-based strategy, because VOCs with the greatest ozone forming potential will be targeted rather than treating each VOC equally.

The reformulation options may be greater with a reactivity-based strategy. At the same time, there should be less tendency for lower reactive solvents to be replaced with higher

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[1] Air Resources Board. Status Report Architectural Coatings Suggested Control Measure. June 2001.
 Air Resources Board. Status Report Architectural Coatings Suggested Control Measure. December 2002.
[2] Air Resources Board. Proposed Regulations for Low-Emission Vehicles and Clean Fuels Staff Report. August 13, 1990.
[3] Air Resources Board. Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products and Proposed Tables of Maximum Incremental Reactivity (MIR) Values, and Proposed Amendments to Method 310, "Determination of Volatile Organic Compounds in Consumer Products." May 5, 2000.

reactive or toxic solvents to lower the total VOC content. For example, we would expect to see less use of some toxic compounds, such as xylene and toluene, because of their high reactivity.

There are also advantages associated with enforceability. There will no longer be a need to consider U.S. EPA's and ARB's exempt VOCs based on negligible reactivity, since the reactivity of all VOCs is counted and nothing is exempt. The "less water and exempts" calculation for determining the VOC content may cease to be an issue, since limits may be expressed in units other than grams of VOC per liter of coating, less water and exempt compounds.

Disadvantages of a Reactivity-Based SCM for Architectural Coatings

There are implications for both the regulatory agencies and the manufacturers if we go forward with a reactivity-based SCM for architectural coatings. Architectural coatings are regulated by the local air districts. Since the districts may be implementing a more complex reactivity-based regulation, the ARB will provide assistance as needed.

Since more than 80 percent of the market is already water-borne, and relatively low reactive mineral spirits dominate the VOCs in solvent-borne coatings, there may not be much opportunity to reformulate with lower-reactive solvents. In addition, we will need to analyze whether acceptable substitutes (on technical, economic, and health impact levels) are available for the highly reactive solvents used in architectural coatings, if mandatory reactivity-based limits are proposed.

Any reactivity-based strategy would evaluate the potential uses of toxic compounds. Because toxic compounds such as methylene chloride and perchloroethylene may have a potential increased use due to their low reactivity, we may need to cap current uses and potentially prevent or minimize new uses of these chemicals.

Chapter 2 – **Reactivity Analysis of Survey Data**

<u>Individual MIR Values</u>

Ozone is created by chemical reactions that occur between organic compounds and nitrogen oxides (NOx), in the presence of sunlight. The reactivity of organic compounds varies widely, depending on the specific chemical and the atmospheric conditions. This reactivity can be characterized in a number of ways, using a variety of measurement scales. ARB has two reactivity-based regulations which are based on the Maximum Incremental Reactivity (MIR) scale developed by Dr. William Carter at the University of California, Riverside. Incremental reactivity is the change in ozone that is caused by adding a small amount of an organic compound to a standard gas mixture. The MIR scale is appropriate for areas that have high NOx concentrations, which is typical for ozone nonattainment areas in California. MIR values are calculated from a computer model that is based on the SAPRC-99 chemical mechanism. Environmental chamber experiments have been conducted to verify and refine the SAPRC-99 mechanism. Additional chamber experiments are ongoing and the mechanism is updated accordingly as new data are gathered.

MIR values have been assigned for hundreds of organic compounds, including both VOCs and exempt compounds. ARB uses the term Reactive Organic Gases (ROG) for VOCs only and the term Total Organic Gases (TOG) to include both VOCs and exempt compounds. MIR values are expressed in units of grams ozone per grams TOG (g O_3/g TOG) and these values are updated periodically by Dr. William Carter.[1] The ARB Executive Officer is planning to conduct a hearing in December 2003 to consider a formal update of the Tables of MIR Values for the Aerosol Coatings Regulation and any other future reactivity regulations.

The MIR scale can be used to assign reactivity values for most of the pure chemicals that are used in architectural coatings. However, hydrocarbon solvents are a major ingredient in architectural coatings and they generally consist of mixtures, rather than pure compounds. For hydrocarbon solvents, ARB developed a bin system in conjunction with the development of the Aerosol Coating regulation.[2] These bins assign MIR values, based on average boiling points and hydrocarbon characteristics (e.g., aromatic content). The bins are similar to the categories contained in the following standards from the American Society for Testing and Materials (ASTM):

D 235: Mineral Spirits (Petroleum Spirits, Hydrocarbon Dry Cleaning Solvent)
D 3734: High-Flash Aromatic Naphthas
D 3735: VM&P Naphthas

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[1] The most recent update prepared by Dr. Carter is dated February 5, 2003 and can be obtained at the following website: http://pah.cert.ucr.edu/~carter/reactdat.htm#update02. These February 2003 MIR values were used for ARB's reactivity analysis in this report.
[2] Air Resources Board. Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products and Proposed Tables of Maximum Incremental Reactivity (MIR)Values. May 2000.

ARB worked with paint manufacturers and solvent suppliers to identify the appropriate bin numbers for the hydrocarbon solvents that were reported in the 2001 Architectural Coatings Survey.

Dr. Carter's MIR scale and the ARB hydrocarbon solvent bins provided MIR values for approximately 87% by weight of the organic compounds reported in the 2001 survey. For the remaining organic compounds, ARB calculated default MIR values that reflected sales-weighted averages of the MIRs that had been identified. Separate default MIR values were calculated for solventborne and waterborne coatings using the following types of compounds: exempt compounds; hydrocarbon solvents; and other organic compounds (non-exempt, non-hydrocarbon solvent). These values are listed in Table 2-1.

Table 2-1: *Default MIR Values*

Type of Compound	Default MIR Values (g O_3/g TOG)	
	Solventborne	*Waterborne*
Exempt Compounds	0.38	0.42
Hydrocarbon Solvents	1.86	1.82
Other (non-exempt, non-hydrocarbon solvent)	0.35 (100% solids) 4.25	2.25

Product-Weighted MIR Values

The Product-Weighted MIR (PWMIR) represents a compilation of MIR values for all of the individual ingredients in a coating. In one approach, which was used in the ARB's aerosol coatings regulation, the product-weighted MIRs for coatings are calculated as follows:

$$[\text{PWMIR, g } O_3/\text{g product}] = [\text{Wt\%}]_1*[\text{MIR}]_1 + [\text{Wt\%}]_2*[\text{MIR}]_2 +…+[\text{Wt\%}]_n*[\text{MIR}]_n$$

where
   $[\text{Wt\%}]_i$ = the weight percent of each ingredient in a coating product (e.g., 0.25 for 25%)
   $[\text{MIR}]_i$ = the MIR value of each ingredient in a coating product, g O_3/g TOG
   n = the total number of ingredients in a coating product

An example is provided below, based on actual survey data that has been altered slightly to protect manufacturer confidentiality:

Ingredient	CAS #	Wt %	MIR (g O_3/g TOG)	[Wt%]*[MIR]
1,2-Propanediol	57-55-6	4%	2.74	0.110
2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate	25265-77-4	2%	0.88	0.018
2-(2-Butoxyethoxy)-Ethanol	112-34-5	4%	2.87	0.115
2-(2-Methoxyethoxy)-Ethanol	111-77-3	3%	2.88	0.086
Water	7732-18-5	54%	0	0
Solids		33%	0	0
TOTAL =		100%		0.33
Product-Weighted MIR = **0.33** grams ozone/gram product				

Sales-Weighted Average MIR Values

To determine sales-weighted average MIR values (SWAMIRs), we used the following equation:

$$SWAMIR = \frac{[Sales]_1*[PWMIR]_1 + [Sales]_2*[PWMIR]_2 +...+[Sales]_n*[PWMIR]_n}{[Sales]_1 + [Sales]_2 +...+[Sales]_n}$$

where

$[Sales, gals]_i$ = the sales of product "i", gallons
$[PWMIR]_i$ = the Product-Weighted MIR value, grams ozone/gram product
n = the total number of coating products

An example is provided below:

Product	PWMIR (g O3/g product)	Sales (gals)	[PWMIR]*[Sales]
#1	0.75	1,000	750
#2	1.16	12,000	13,920
#3	0.98	3,500	3,430
#4	0.35	500	175
TOTALS:		17,000	18,275
Sales-Weighted Avg. MIR = (18,275)/(17,000) = **1.08** grams ozone/gram product			

SWAMIRs were calculated for all of the coating categories based on the 2001 survey data. The survey collected sales data for more than 8,000 products and it also gathered data on the chemical ingredients contained in each product. However, there were approximately 100 products for which no ingredient data were submitted. These 100 products only represent 2.0% of the total sales volume. Since ingredient data are required to identify MIRs, we did not include the products with missing ingredient data when calculating sales-weighted average MIR values.

Table 2-2 contains overall SWAMIRs for all coatings in a given category. It also contains SWAMIRs for compliant and non-compliant coatings, based on the VOC limits contained in ARB's 2000 Architectural Coatings SCM.

Table 2-2: *SWAMIRs for All Categories*

Coating Category	SCM VOC Limit (g/l)	SWAMIR (g O3/g product)		
		Compliant w/SCM Limit	Non-Compliant	Overall
Antenna	530	0.74	N/A	0.74
Bituminous Roof	300	0.19	0.55	0.20
Bituminous Roof Primer	350	0.29	0.60	0.37
Bond Breakers	350	0.14	0.82	0.16
Clear Brushing Lacquer	680	1.51	N/A	1.51
Concrete Curing Compounds	350	0.19	1.09	0.20
Dry Fog	400	0.24	0.42	0.24
Faux Finishing	350	0.18	0.76	0.23
Fire Resistive	350	0.04	N/A	0.04
Fire Retardant - Clear	650	0.00	N/A	0.00
Fire Retardant - Opaque	350	0.12	1.72	0.13
Flat	**100**	**0.05**	**0.11**	**0.06**
Floor	250	0.18	0.44	0.19
Flow	420	0.54	N/A	0.54
Form Release Compounds	250	0.27	0.93	0.27
Graphic Arts	500	0.45	0.50	0.45
High Temperature	420	0.72	1.92	0.84
Industrial Maintenance	**250**	**0.33**	**0.85**	**0.69**
Lacquers	**550**	**0.59**	**1.67**	**1.34**
Low Solids	120	0.17	N/A	0.17
Magnesite Cement	450	2.12	N/A	2.12
Mastic Texture	300	0.09	0.31	0.11
Metallic Pigmented	500	1.38	3.38	1.40
Multi-Color	250	0.07	1.19	0.33
Nonflat - High Gloss	**250**	**0.25**	**0.63**	**0.34**
Nonflat - Low Gloss	**150**	**0.08**	**0.16**	**0.10**
Nonflat - Medium Gloss	**150**	**0.08**	**0.19**	**0.14**
Other	100	0.00	0.77	0.00
Pre-Treatment Wash Primer	420	0.22	1.43	0.24
Primer, Sealer, and Undercoater	**200**	**0.09**	**0.50**	**0.17**
Quick Dry Enamel	**250**	**0.22**	**0.58**	**0.53**
Quick Dry Primer, Sealer, and Undercoater	**200**	**0.12**	**0.51**	**0.40**
Recycled	250	0.01	0.03	0.02
Roof	250	0.06	0.75	0.09
Rust Preventative	400	0.43	0.44	0.43

Table 2-2: *SWAMIRs for All Categories*

Coating Category	SCM VOC Limit (g/l)	SWAMIR (g O3/g product)		
		Compliant w/SCM Limit	Non-Compliant	Overall
Sanding Sealers	350	0.17	1.33	1.01
Shellacs - Clear	730	1.14	N/A	1.14
Shellacs - Opaque	550	0.74	N/A	0.74
Specialty Primer, Sealer, and Undercoater	350	0.12	0.58	0.14
Stains - Clear/Semitransparent	**250**	**0.10**	**0.61**	**0.55**
Stains - Opaque	**250**	**0.11**	**0.43**	**0.19**
Swimming Pool	340	0.68	1.17	0.71
Swimming Pool Repair and Maintenance	340	N/A	3.56	3.56
Traffic Marking	**150**	**0.07**	**0.45**	**0.08**
Varnishes - Clear	350	0.46	0.73	0.59
Varnishes - Semitransparent	350	0.22	0.53	0.51
Waterproofing Concrete/Masonry Sealers	400	0.26	1.79	0.40
Waterproofing Sealers	**250**	**0.14**	**0.56**	**0.41**
Wood Preservatives	350	0.65	1.17	0.70

Bold highlighting indicates major categories that were targeted for lower VOC limits in ARB's 2000 SCM.
"N/A": Not applicable, because there were no coatings in this compliance category.

Figure 2-1 contains the SWAMIRs and the associated sales for selected categories that were targeted for lower VOC limits in ARB's 2000 Suggested Control Measure.

**Figure 2-1: Selected Categories
Sales-Weighted Average MIR and 2000 Sales Data**
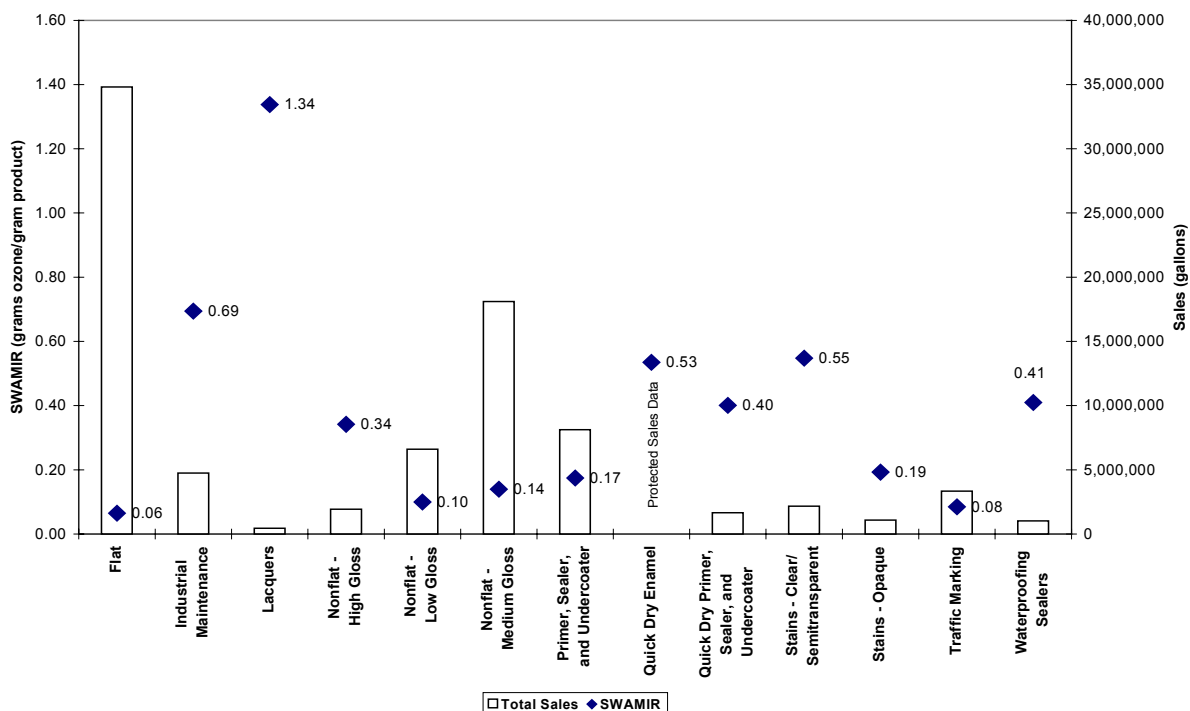
Figures 2-2 to 2-14 contain charts of the SWAMIRs for selected categories in 50-gram/liter (g/l) ranges, along with the associated sales values in each range.

Figure 2-2: Flat
Sales-Weighted Average MIR and 2000 Sales Data
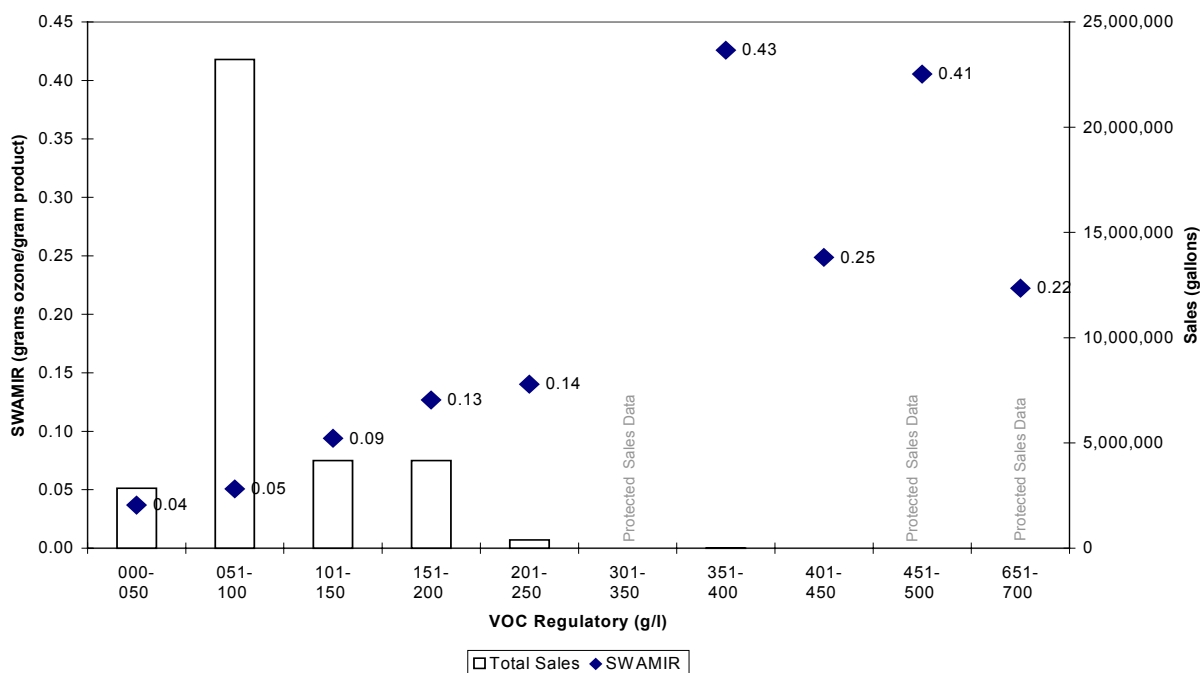
No MIR value could be calculated for Flats in the 301-350 g/l range, because no ingredient data were provided.

Figure 2-3: Industrial Maintenance
Sales-Weighted Average MIR and 2000 Sales Data
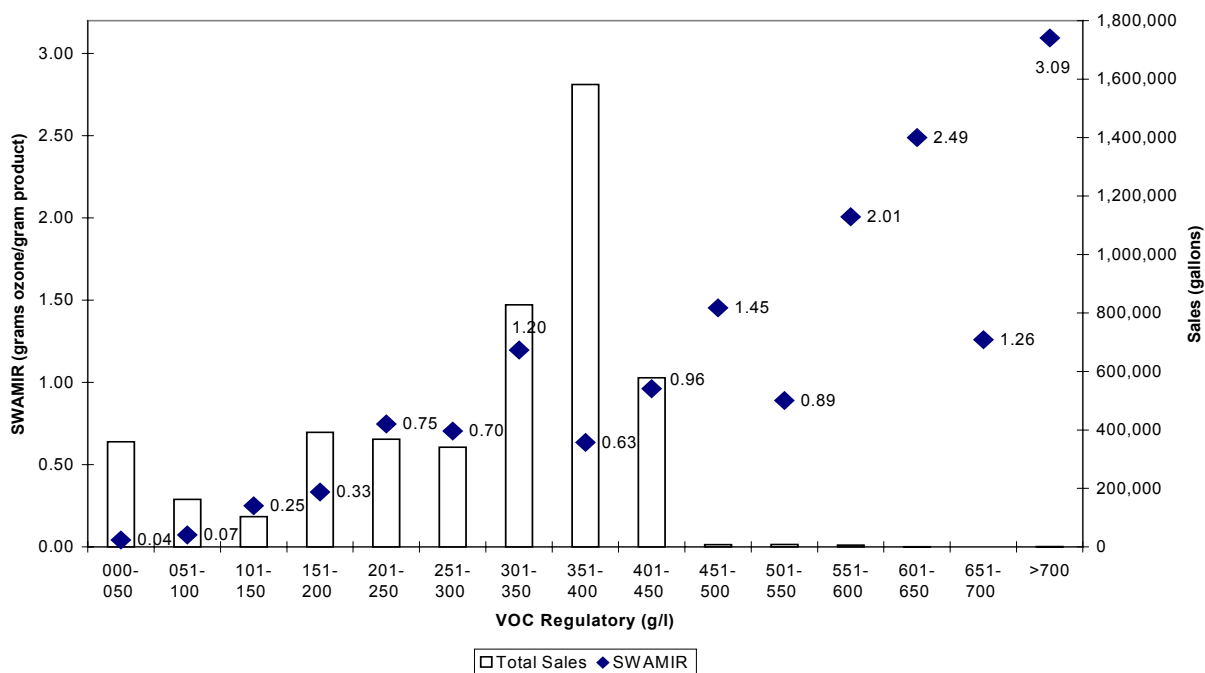
Figure 2-4: Lacquers
Sales-Weighted Average MIR and 2000 Sales Data
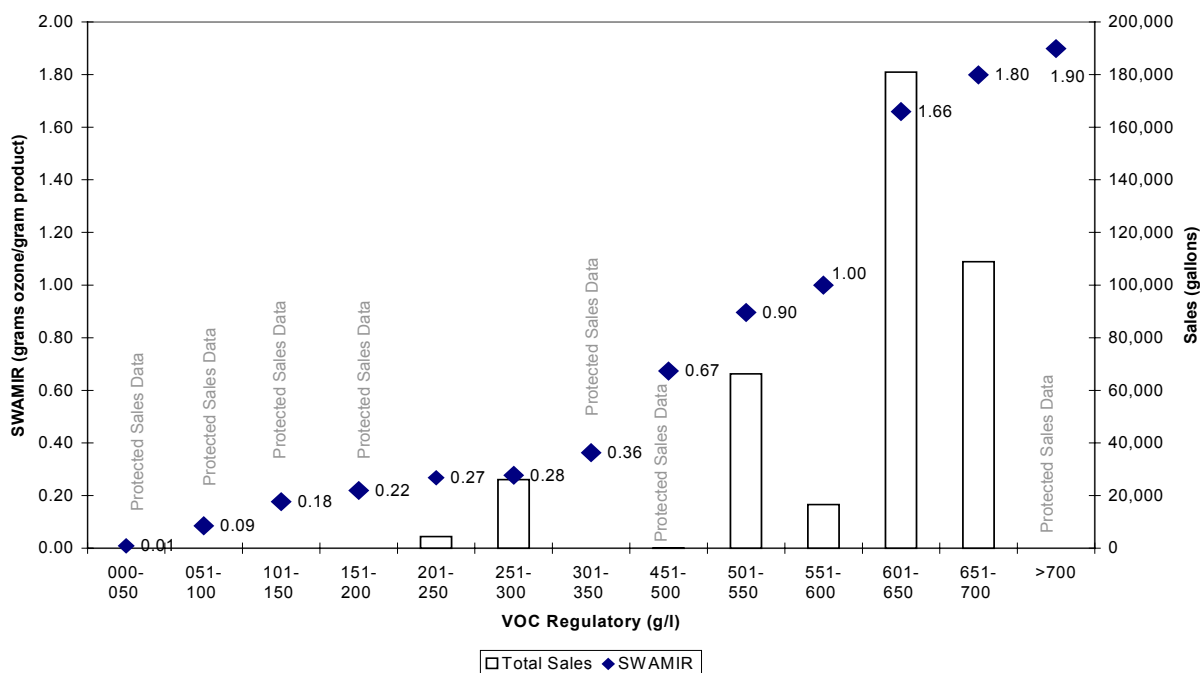
Figure 2-5: Nonflat - High Gloss
Sales-Weighted Average MIR and 2000 Sales Data
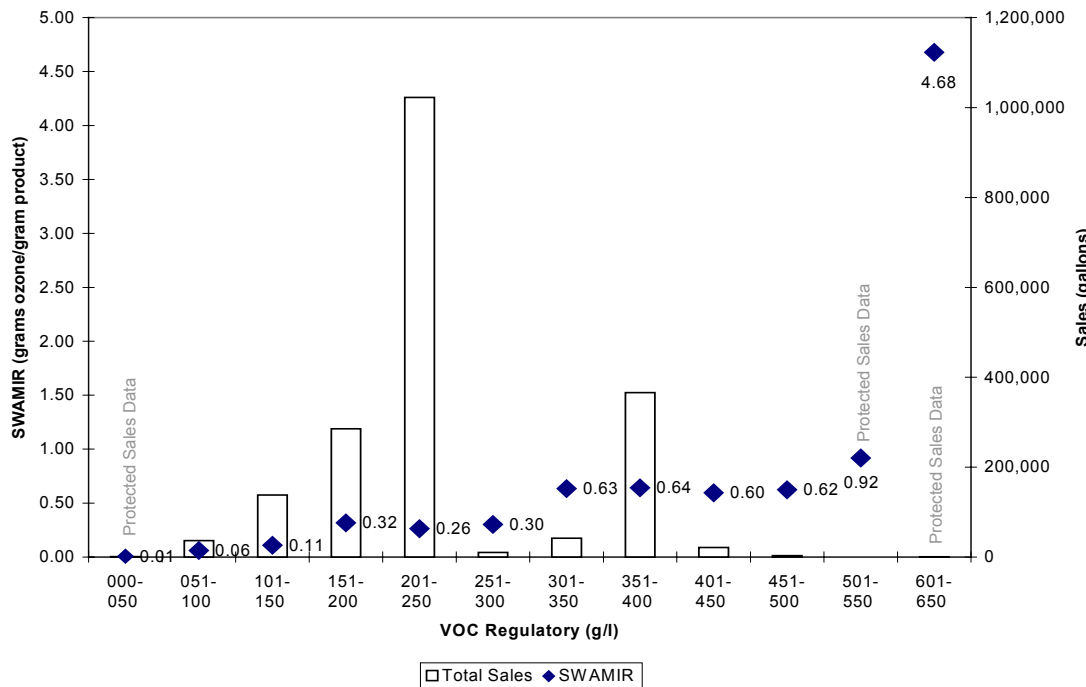
Figure 2-6: Nonflat - Low Gloss
Sales-Weighted Average MIR and 2000 Sales Data
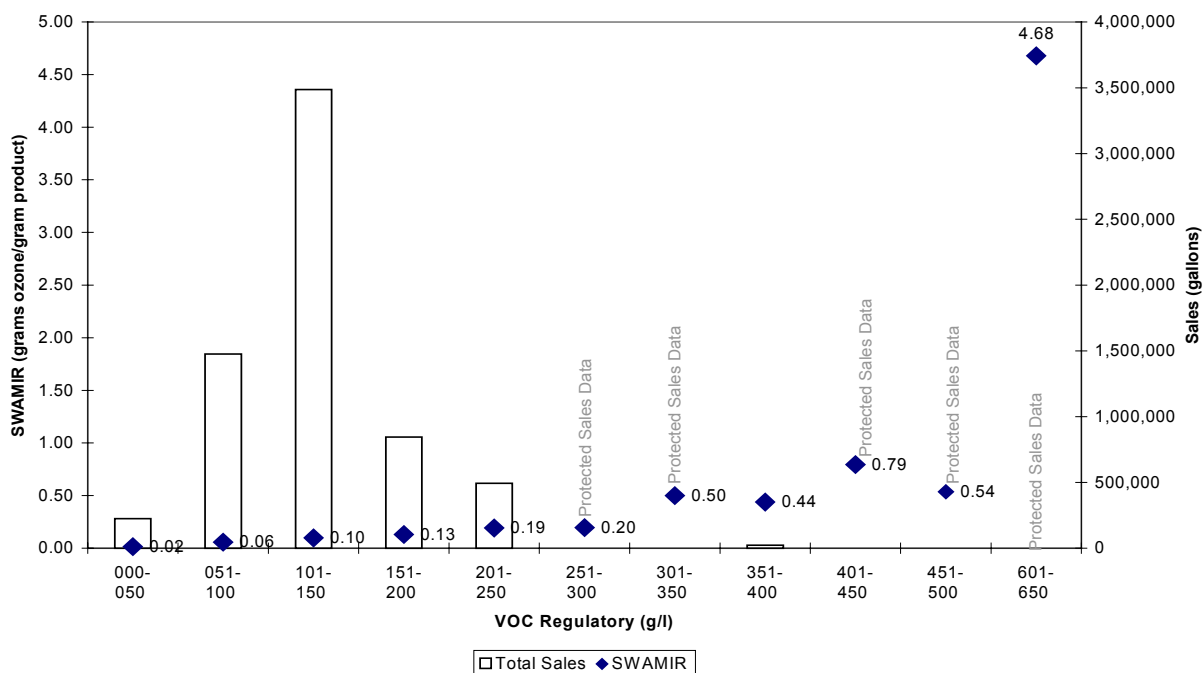
Figure 2-7: Nonflat - Medium Gloss
Sales-Weighted Average MIR and 2000 Sales Data
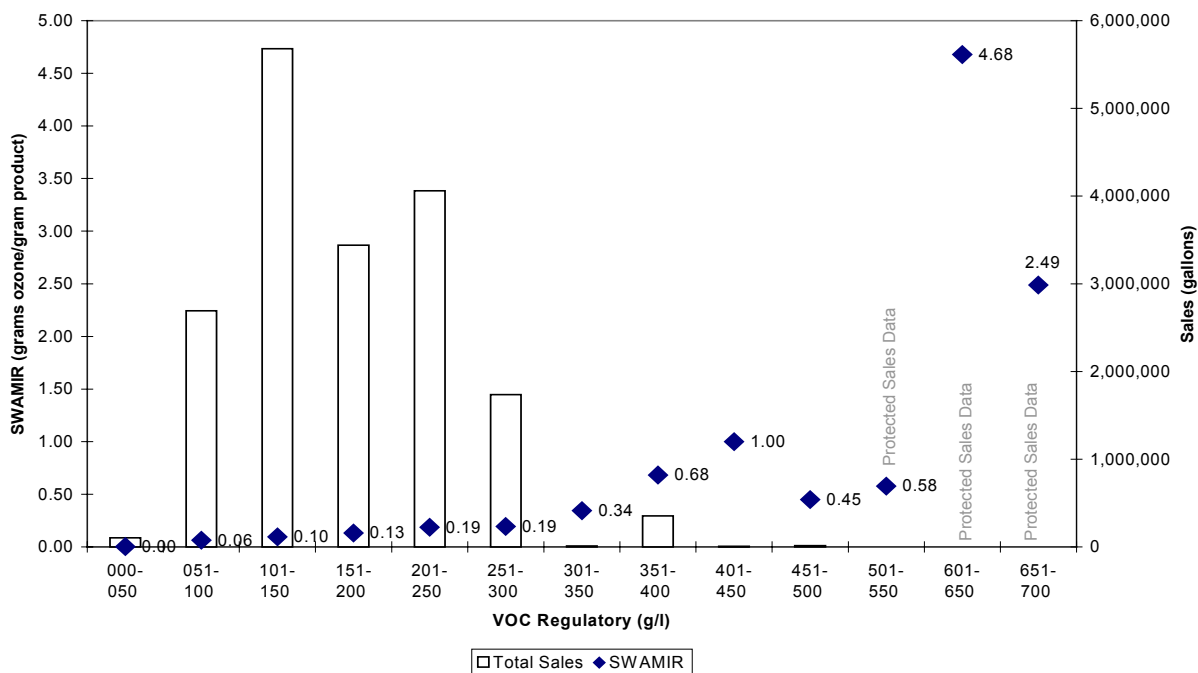
Figure 2-8: Primer, Sealer, Undercoater
Sales-Weighted Average MIR and 2000 Sales Data
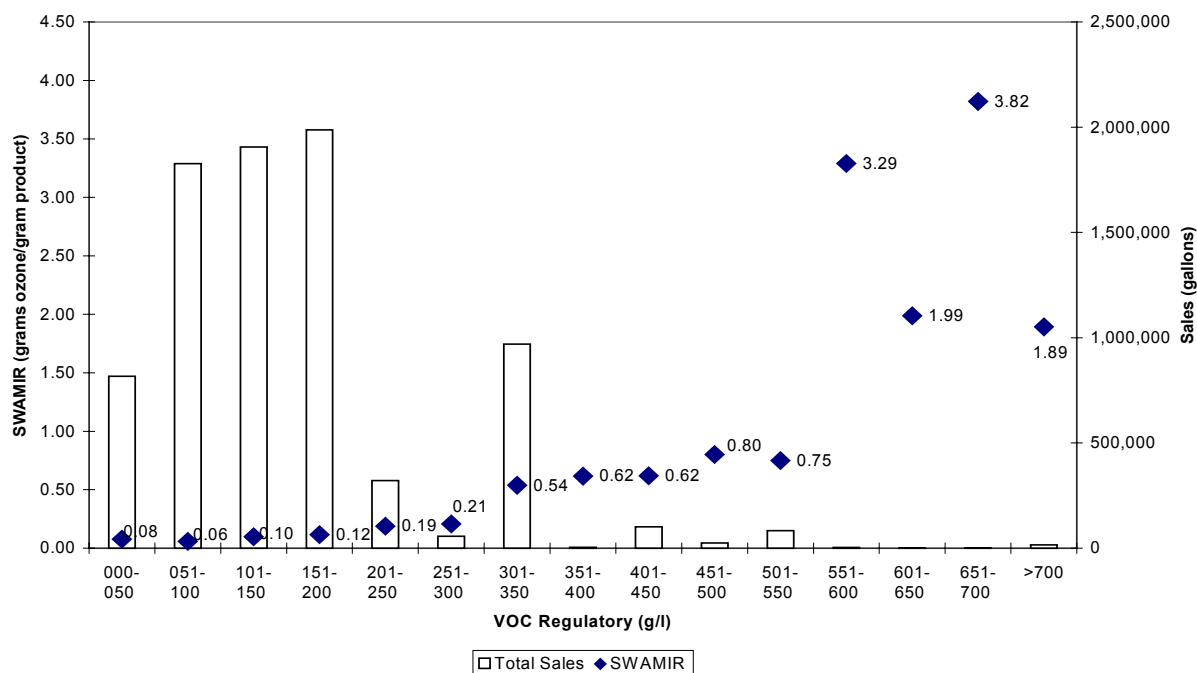
Figure 2-9: Quick Dry Enamel
Sales-Weighted Average MIR and 2000 Sales Data
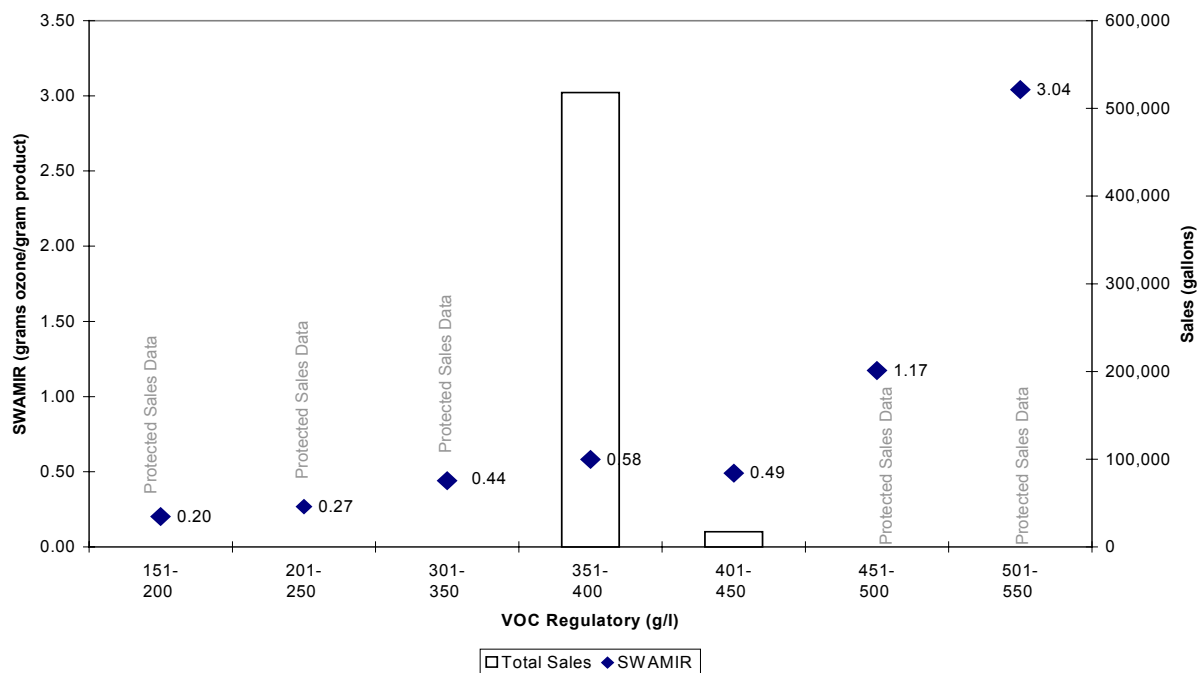
Figure 2-10: Quick Dry Primer, Sealer, Undercoater
Sales-Weighted Average MIR and 2000 Sales Data
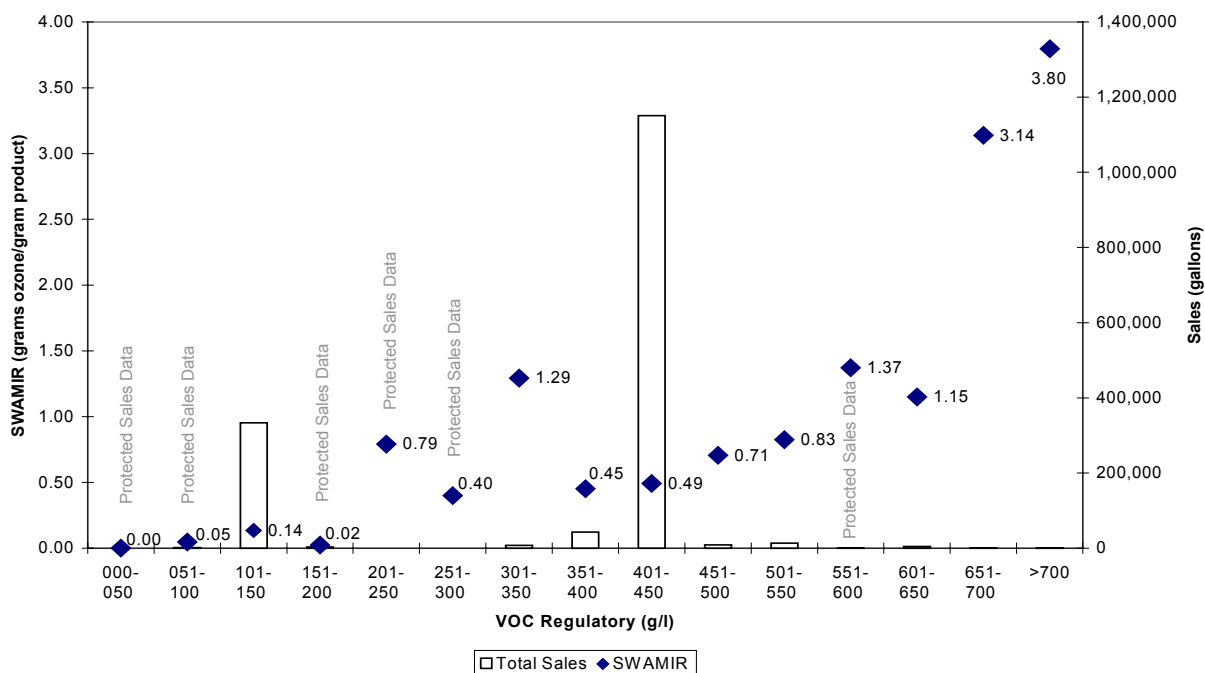
Figure 2-11: Stain - Clear/Semitransparent
Sales-Weighted Average MIR and 2000 Sales Data
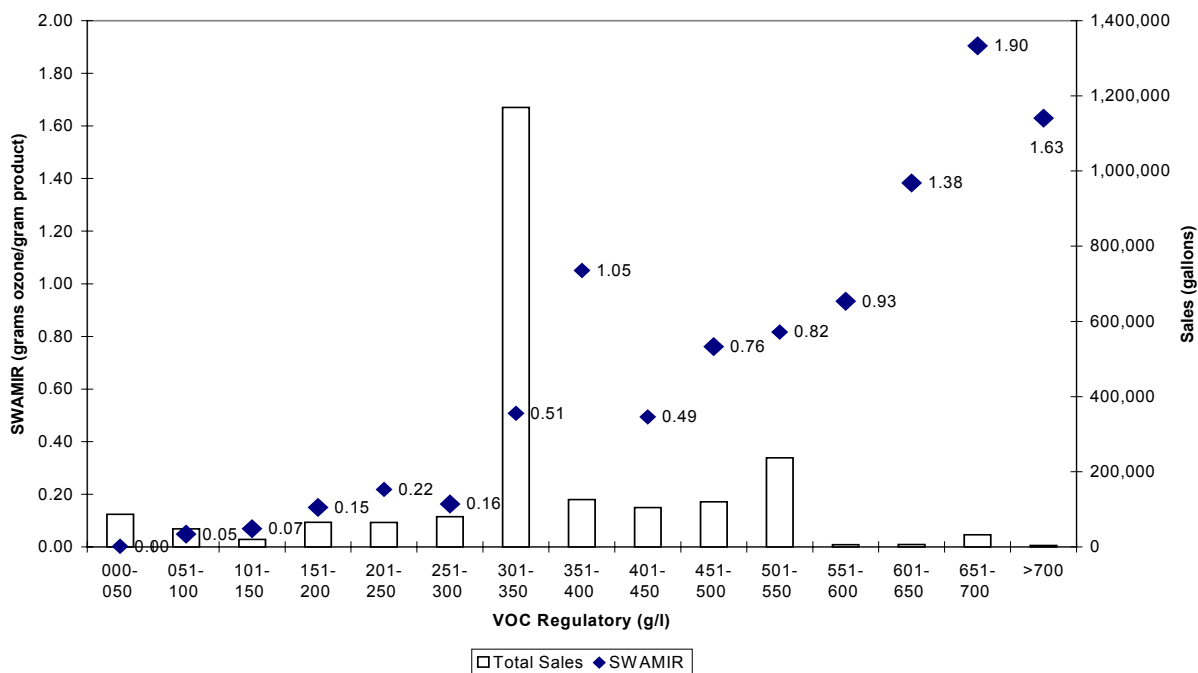
Figure 2-12: Stain - Opaque
Sales-Weighted Average MIR and 2000 Sales Data
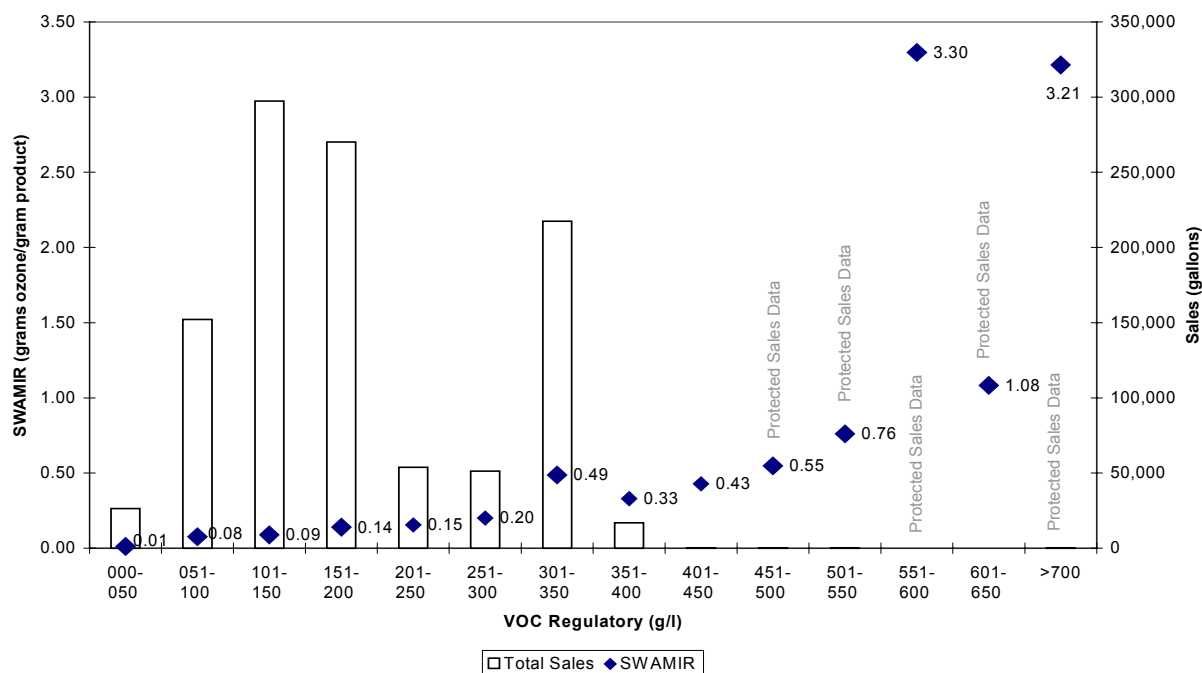
Figure 2-13: Traffic Marking
Sales-Weighted Average MIR and 2000 Sales Data
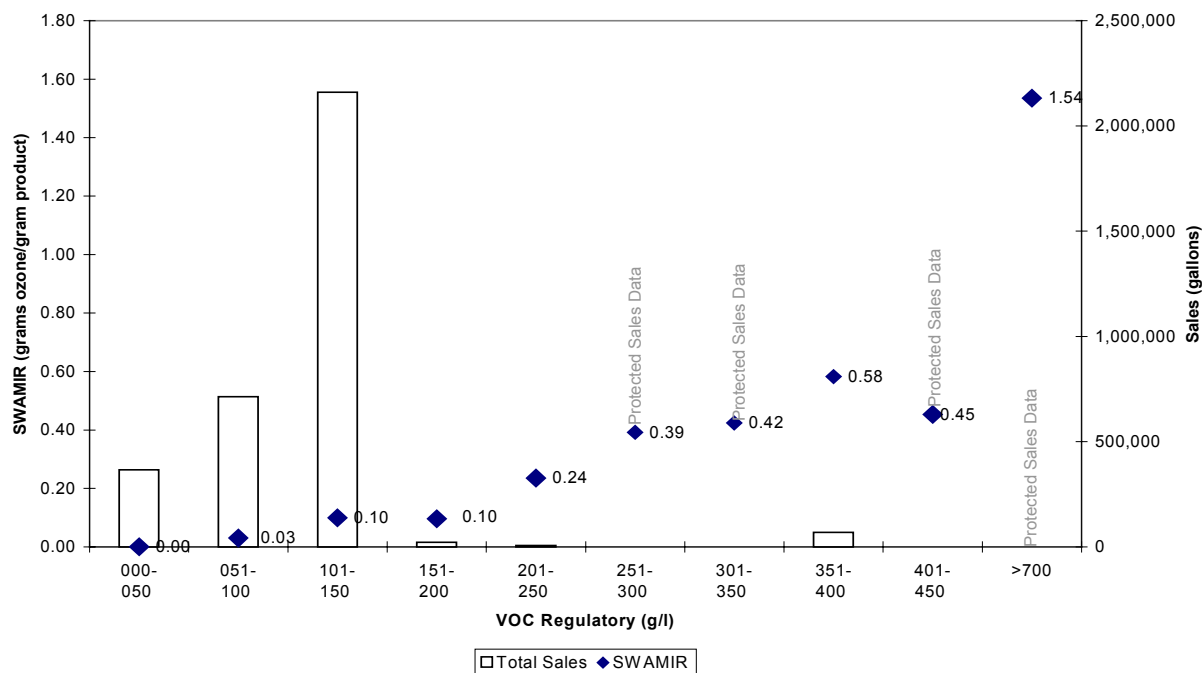
Figure 2-14: Waterproofing Sealers
Sales-Weighted Average MIR and 2000 Sales Data
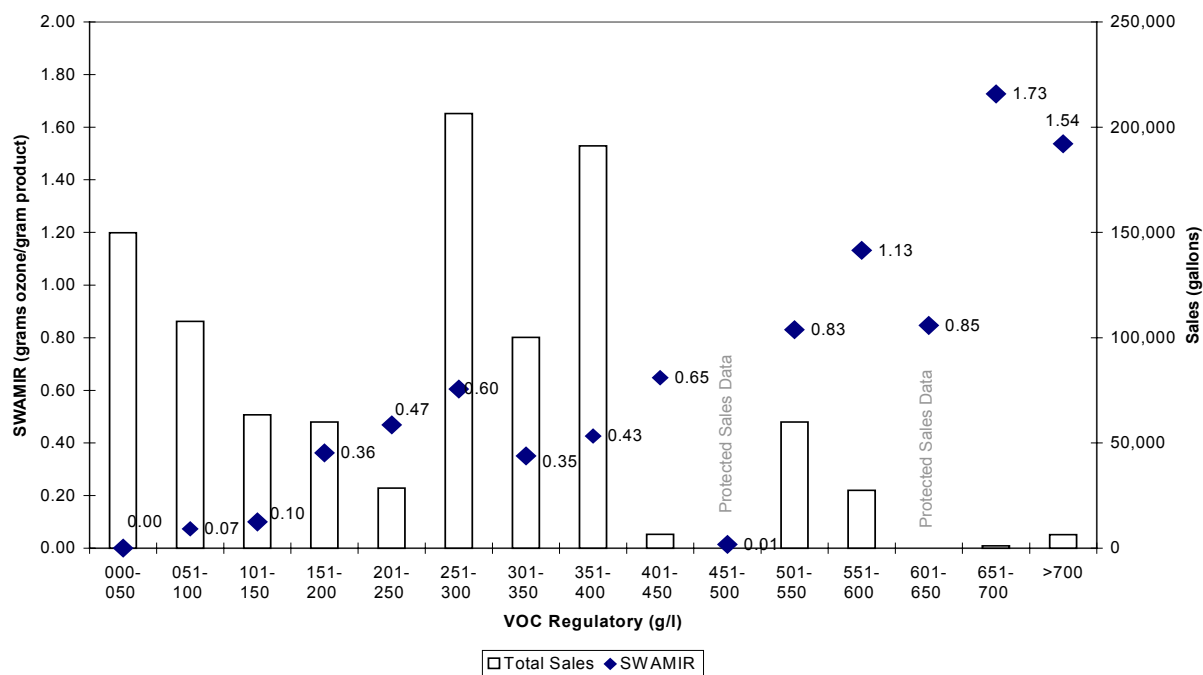
Table 2-3 contains SWAMIRs that were calculated for 50-g/l ranges for all categories. Sales-weighted averages were calculated based on sales volumes (gallons).

Table 2-3: *Sales-Weighted Average MIR Values in 50-g/l Ranges (grams ozone/gram product)*

| Coating Category	VOC Ranges (grams/liter)														
	0-50	51-100	101-150	151-200	201-250	251-300	301-350	351-400	401-450	451-500	501-550	551-600	601-650	651-700	> 700
Antenna						0.36		1.37		0.73					
Bituminous Roof	0.00	0.07	0.14	0.28	0.38	0.50	0.52	0.94		0.43					
Bituminous Roof Primer	0.06			0.20			0.84		0.60						
Bond Breakers		0.08		0.06		0.08	0.19					0.82			
Clear Brushing Lacquer														1.51	
Concrete Curing Compounds	0.06	0.07	0.11	0.21	0.10	0.17	1.12			0.01	0.49	1.35	3.68	5.39	1.66
Dry Fog	0.02	0.04	0.08	0.07		0.25	0.30	0.37	0.40		0.82				
Faux Finishing		0.06	0.10		0.20	0.24	0.23	0.31	0.51					0.78	0.95
Fire Resistive	0.04														
Fire Retardant - Clear	0.00														
Fire Retardant - Opaque	0.02	0.04	0.08		1.09	1.04	0.89			0.98		3.91			4.82
Flat	0.04	0.05	0.09	0.13	0.14			0.43	0.25	0.41				0.22	
Floor	0.17	0.06	0.24	0.16	0.25	0.27	0.27	0.64	0.89	0.50	1.05		1.09		
Flow									0.54						
Form Release Compounds		0.07	0.05	0.40	0.31		0.74		0.94						
Graphic Arts		0.03	0.10	0.22	0.28	0.32	0.30	0.86	0.64		0.50				
High Temperature						0.58	0.52	0.78	0.58	1.23	2.54	2.94	1.85	2.88	
Industrial Maintenance	0.04	0.07	0.25	0.33	0.75	0.70	1.20	0.63	0.96	1.45	0.89	2.01	2.49	1.26	3.09
Lacquers	0.01	0.09	0.18	0.22	0.27	0.28	0.36			0.67	0.90	1.00	1.66	1.80	1.90
Low Solids	0.05	0.23													
Magnesite Cement									2.12						
Mastic Texture	0.01	0.08	0.19	0.17	0.12	0.37		0.31							
Metallic Pigmented		0.25	0.08	0.22	0.35	0.84	0.62	0.92	0.82	1.96	1.15	1.74	2.54	4.49	4.59
Multi-Color		0.02	0.10		0.18					0.24	0.43				2.02
Nonflat - High Gloss	0.01	0.06	0.11	0.32	0.26	0.30	0.63	0.64	0.60	0.62	0.92		4.68		
Nonflat - Low Gloss	0.02	0.06	0.10	0.13	0.19	0.20	0.50	0.44	0.79	0.54			4.68		

Table 2-3: *Sales-Weighted Average MIR Values in 50-g/l Ranges (grams ozone/gram product)*

Coating Category	VOC Ranges (grams/liter)														
	0-50	51-100	101-150	151-200	201-250	251-300	301-350	351-400	401-450	451-500	501-550	551-600	601-650	651-700	> 700
Nonflat - Medium Gloss	0.00	0.06	0.10	0.13	0.19	0.19	0.34	0.68	1.00	0.45	0.58		4.68	2.49	
Other	0.00	0.18	0.02		0.95	0.42	0.37				0.60	1.68		0.78	
Pre-Treatment Wash Primer	0.07	0.07	0.07				0.29	0.29						1.03	1.83
Primer, Sealer, and Undercoater	0.08	0.06	0.10	0.12	0.19	0.21	0.54	0.62	0.62	0.80	0.75	3.29	1.99	3.82	1.89
Quick Dry Enamel				0.20	0.27		0.44	0.58	0.49	1.17	3.04				
Quick Dry Primer, Sealer, and Undercoater	0.00	0.05	0.14	0.02	0.79	0.40	1.29	0.45	0.49	0.71	0.83	1.37	1.15	3.14	3.80
Recycled					0.03	0.03									
Roof	0.03	0.08	0.18	0.15	0.29	0.64	0.72		1.17						1.79
Rust Preventative		0.04	0.11	0.14	0.22	1.25	1.36	0.41	0.64	0.42					1.34
Sanding Sealers				0.14	0.18	0.20	0.17				0.93	1.80		1.04	2.43
Shellacs - Clear												0.90	1.21	1.12	
Shellacs - Opaque											0.74				
Specialty Primer, Sealer, and Undercoater	0.03	0.11	0.09	0.15	0.23	0.60	0.35		0.58	0.87				1.61	
Stains - Clear/Semitransparent	0.00	0.05	0.07	0.15	0.22	0.16	0.51	1.05	0.49	0.76	0.82	0.93	1.38	1.90	1.63
Stains - Opaque	0.01	0.08	0.09	0.14	0.15	0.20	0.49	0.33	0.43	0.55	0.76	3.30	1.08		3.21
Swimming Pool	0.04	0.08	0.08	0.20	0.45	1.09	1.13		1.19		0.48				
Swimming Pool Repair and Maintenance												3.56			
Traffic Marking	0.00	0.03	0.10	0.10	0.24	0.39	0.42	0.58	0.45						1.54
Varnishes - Clear		0.09	0.16	0.14	0.21	0.31	0.68	0.62	0.69	0.73	0.73	1.16		1.55	1.75
Varnishes - Semitransparent					0.22	0.23	0.18	0.29	0.52	1.11	1.94				
Waterproofing Concrete/Masonry Sealers	0.00	0.08	0.10	0.19	0.85	0.21	0.26	0.75	0.74		0.79	3.99		1.81	1.65
Waterproofing Sealers	0.00	0.07	0.10	0.36	0.47	0.60	0.35	0.43	0.65	0.01	0.83	1.13	0.85	1.73	1.54
Wood Preservatives	0.06	0.30	0.10	0.11	0.31	0.26	0.68		0.48	0.72	1.22			1.13	1.67

Blank cells indicate that the SWAMIR could not be calculated for this VOC range, because there were no sales or the Form 3 ingredient data was incomplete.

Some members of the architectural coatings industry have indicated that the PWMIR and SWAMIR approach is appropriate for regulating aerosol coatings, but they do not believe this approach is suitable for architectural coatings. One option presented by one manufacturer involves a reactivity-adjusted VOC content, which is a VOC content that has been adjusted to account for the reactivity of the individual VOCs and exempt compounds that are contained in a coating. If a coating has a large amount of highly reactive compounds, the reactivity-adjusted VOC content could be higher than the traditional VOC content. An advantage of this approach is the retention of measurement units (grams/liter or lbs/gal) that are already familiar to manufacturers and coating users. This approach and others are discussed below. We will be working with the industry and local air districts as we consider various approaches and methods to evaluate a reactivity-based control measure for architectural coatings.

Reactivity-Adjusted VOC Values

ARB worked with coating manufacturers to obtain input on alternative methods for describing the reactivity of architectural coatings. One manufacturer suggested that the VOC Regulatory value be adjusted to reflect the relative reactivity of the VOCs contained in the coating. Relative reactivity could be defined as the ratio of the reactivity for the VOC species to the reactivity for the Base Case ROG Mixture[3]. A coating's VOC Regulatory value could be multiplied by the relative reactivity to obtain a reactivity-adjusted VOC content, as described below.

To determine Reactivity-Adjusted VOCs (RAVOCs), we used the following equations:

1) Calculate the relative reactivity for each VOC and exempt compound in a coating:

[Relative Reactivity (RRi)] = [MIRi]/[MIRBC]

where
   MIRi = the MIR of each VOC or exempt compound in a product, grams ozone/grams TOG
   MIRBC = the MIR of the Base Case ROG Mixture = 3.71 grams ozone/grams TOG

2) Determine the Reactivity Adjustment Factor (RAF) for the coating:

$$RAF = \frac{[RR]_1 * [Wt\%]_1 + [RR]_2 * [Wt\%]_2 + \ldots + [RR]_n * [Wt\%]_n}{[Total\ Wt\%]}$$

where
   [RR]i = the relative reactivity of each VOC or exempt compound in a coating
   [Wt%]i = the weight percent of each VOC or exempt compound in a coating
   [Total Wt%] = the total weight percent of all VOCs and exempt compounds in a product

3) Calculate the Reactivity-Adjusted VOC (RAVOC) for a coating:

[RAVOC, g/l] = [VOC Regulatory Content, g/l]*[RAF]

[3] The Base Case ROG mixture is a mixture of reactive organic gases that represents the chemical composition of the air in 39 urban areas throughout the United States. The U.S. Environmental Protection Agency selected a high ozone episode from each of these 39 areas to establish a geographically representative distribution of conditions in ozone nonattainment areas.

An example is provided below, based on actual survey data that has been altered slightly to protect manufacturer confidentiality:

n	Ingredient	MIR Value (g O₃/g TOG)	RRi	[Wt%]ᵢ	[RR]ᵢ*[Wt%]ᵢ [Total Wt%]
1	Mineral Spirits (Bin 14)	1.21	0.33	35	0.27
2	Mineral Spirits (Bin 11)	0.91	0.25	4	0.02
3	Propylene Glycol	2.74	0.74	2	0.04
4	Xylene	7.48	2.02	1	0.05
				Total Wt% = 42%	**RAF = 0.38**
VOC Regulatory Content = 550 g/l **RAVOC** = [0.38]*[550 g/l] = **208 g/l**					

Determining the reactivity-adjusted VOC content can provide a mechanism for identifying coatings that contain highly reactive VOCs, but it doesn't really reflect the overall reactivity of a coating because it does not account for the presence of water and solids. Focusing only on VOCs can make a coating seem highly reactive, when it contains a relatively small quantity of VOCs. Consider the following example for two coatings, one solventborne and one waterborne, that both have a VOC Regulatory value of 280 g/l. If the reactivity adjustment factor is based only on VOCs and exempt compounds, it appears that the waterborne compound has a significantly higher RAVOC than the solventborne coating. However, if the reactivity adjustment factor is based on all of the ingredients in the coating, the solventborne coating has a higher RAVOC than the waterborne coating, as shown below:

	Reactivity Adjustment Factor		VOC Regulatory (g/l)	Reactivity Adjusted VOC	
	Based on VOCs & Exempts Only	Based on All Ingredients		Based on VOCs & Exempts Only	Based on All Ingredients
Solventborne	0.45	0.14	280	126	39
Waterborne	0.89	0.10	280	250	28

Details of this analysis are provided in the following summaries, which are based on actual survey data that has been altered slightly to protect manufacturer confidentiality:

Solventborne Coating: Reactivity Adjusted VOC – Based on VOCs and Exempts Only

n	Ingredient	MIR Value (g O₃/g TOG)	RRi	[Wt%]ᵢ	[RR]ᵢ*[Wt%]ᵢ [Total Wt%]
1	HC Solvent (Bin 14)	1.21	0.33	19.3	0.21
2	Aromatic 100	7.51	2.02	1.3	0.09
3	HC Solvent (Bin unknown)	1.86	0.50	9.2	0.15
				Total Wt% = 29.8%	**RAF = 0.45**
VOC Regulatory Content = 280 g/l **RAVOC** = [0.45]*[280 g/l] = **126 g/l**					

Solventborne Coating: Reactivity Adjusted VOC – Based on All Ingredients

n	Ingredient	MIR Value (g O_3/g TOG)	RRi	[Wt%]$_i$	$\frac{[RR]_i*[Wt\%]_i}{[Total\ Wt\%]}$
1	HC Solvent (Bin 14)	1.21	0.33	19.3	0.06
2	Aromatic 100	7.51	2.02	1.3	0.03
3	HC Solvent (Bin unknown)	1.86	0.50	9.2	0.05
4	Solids	0	0	70.2	0
				Total Wt% = 100%	**RAF = 0.14**
VOC Regulatory Content = 280 g/l					
RAVOC = [0.14]*[280 g/l] = **39 g/l**					

Waterborne Coating: Reactivity Adjusted VOC – Based on VOCs and Exempts Only

n	Ingredient	MIR Value (g O_3/g TOG)	RRi	[Wt%]$_i$	$\frac{[RR]_i*[Wt\%]_i}{[Total\ Wt\%]}$
1	2-Propoxyethanol	3.50	0.94	5.7	0.48
2	2-Butoxyethanol	2.88	0.78	4.4	0.31
3	Toluene	3.97	1.07	1.0	0.10
				Total Wt% = 11.1%	**RAF = 0.89**
VOC Regulatory Content = 280 g/l					
RAVOC = [0.89]*[280 g/l] = **250 g/l**					

Waterborne Coating: Reactivity Adjusted VOC – Based on All Ingredients

n	Ingredient	MIR Value (g O_3/g TOG)	RRi	[Wt%]$_i$	$\frac{[RR]_i*[Wt\%]_i}{[Total\ Wt\%]}$
1	2-Propoxyethanol	3.50	0.94	5.7	0.05
2	2-Butoxyethanol	2.88	0.78	4.4	0.03
3	Toluene	3.97	1.07	1.0	0.01
4	Water	0	0	37.3	0
5	Solids	0	0	51.6	0
				Total Wt% = 100%	**RAF = 0.10**
VOC Regulatory Content = 280 g/l					
RAVOC = [0.10]*[280 g/l] = **28 g/l**					

Table 2-4 contains a listing of the sales-weighted average VOC Regulatory values and the corresponding Reactivity-Adjusted VOC values for each coating category. The RAVOC has been calculated using two different methods. For one method, the reactivity adjustment factor is calculated based on VOCs and exempt compounds only. The other method uses a reactivity adjustment factor that is based on all of the ingredients in the coating, which results in a value that reflects the overall reactivity of the coatings.

When calculating RAVOC, based on VOCs and exempt compounds only, the value is almost always less than the standard VOC Regulatory content. This is due to the fact that the reactivity adjustment factor includes the ratio of individual chemical MIRs to the MIR for the Base Case ROG Mixture. The MIR value for the Base Case ROG Mixture is 3.71 grams ozone/gram ROG, which is generally higher than the MIR values for the ingredients that are used in coatings. Therefore, the ratio is usually less than one and the resulting RAVOC is less than the VOC Regulatory content.

Table 2-4: *SWA Reactivity-Adjusted VOCs for All Categories*

Coating Category	SWA VOC Reg. (g/l)	SWA RAVOC (g/l)	
		Based on VOCs & Exempts Only	Based on All Ingredients
Antenna	433	291	87
Bituminous Roof	120	54	14
Bituminous Roof Primer	211	127	35
Bond Breakers	244	194	15
Clear Brushing Lacquer	667	366	271
Concrete Curing Compounds	145	149	13
Dry Fog	258	117	23
Faux Finishing	261	173	25
Fire Resistive	45	25	0
Fire Retardant - Clear	4	2	0
Fire Retardant - Opaque	94	73	8
Flat	96	55	2
Floor	101	67	7
Flow	412	319	60
Form Release Compounds	213	66	17
Graphic Arts	274	163	46
High Temperature	401	259	96
Industrial Maintenance	298	242	64
Lacquers	567	385	223
Low Solids	59	47	3
Magnesite Cement	443	481	253
Mastic Texture	133	67	5
Metallic Pigmented	409	420	182
Multi-Color	227	239	56
Nonflat – High Gloss	244	157	26
Nonflat – Low Gloss	129	82	4
Nonflat – Medium Gloss	171	105	8
Other	1	1	0
Pre-Treatment Wash Primer	252	168	23
Primer, Sealer, and Undercoater	155	100	13
Quick Dry Enamel	358	176	54
Quick Dry Primer, Sealer, and Undercoater	364	162	44
Recycled	204	65	1
Roof	68	45	4
Rust Preventative	339	172	42
Sanding Sealers	471	270	151
Shellacs – Clear	600	273	185
Shellacs – Opaque	538	248	107
Specialty Primer, Sealer, and Undercoater	120	86	7
Stains – Clear/Semitransparent	349	160	60
Stains – Opaque	180	113	13
Swimming Pool	274	315	60
Swimming Pool Repair and Maintenance	573	1,077	552
Traffic Marking	116	34	4

Table 2-4: *SWA Reactivity-Adjusted VOCs for All Categories*

Coating Category	SWA VOC Reg. (g/l)	SWA RAVOC (g/l)	
		Based on VOCs & Exempts Only	Based on All Ingredients
Varnishes - Clear	375	181	66
Varnishes - Semitransparent	431	131	60
Waterproofing Concrete/Masonry Sealers	209	153	48
Waterproofing Sealers	251	148	40
Wood Preservatives	345	177	70

Composite Average MIR for VOC and Exempt Compounds

Another type of reactivity analysis that was recommended by one manufacturer involves determining an average MIR value for the VOCs and exempt compounds that are contained in a coating. This type of parameter characterizes the reactivity of the solvents in a coating, but it doesn't necessarily correspond to the overall reactivity of a coating. If a product only contains a small percentage of a solvent blend that has a high composite MIR, the impact of that solvent blend may be relatively small and the overall reactivity of the coating could still be low.

To determine the Composite MIR (CMIR), we used the following equation:

$$CMIR = \frac{[MIR]_1 * [Wt\%]_1 + [MIR]_2 * [Wt\%]_2 + \ldots + [MIR]_n * [Wt\%]_n}{[Total\ Wt\%]}$$

where

MIR_i = the MIR of each VOC or exempt compound in a product, grams ozone/grams product
$[Wt\%]_i$ = the weight percent of each VOC or exempt compound in a coating
$[Total\ Wt\%]$ = the total weight percent of all VOCs and exempt compounds in a product

An example is provided below, based on actual survey data that has been altered slightly to protect manufacturer confidentiality:

n	Ingredient	MIR Value (g O_3/g TOG)	$[Wt\%]_i$	$\frac{[MIR]_i*[Wt\%]_i}{[Total\ Wt\%]}$
1	Mineral Spirits (Bin 14)	1.21	35	1.01
2	Mineral Spirits (Bin 11)	0.91	4	0.09
3	Propylene Glycol	2.74	2	0.13
4	Xylene	7.48	1	0.18
			Total Wt% = 42%	**CMIR = 1.41**

Table 2-5 contains a listing of the sales-weighted average composite average MIR values (SWA CMIR) for the VOCs and exempt compounds contained in each coating category. The table also lists those compounds that were the primary contributors to the SWA CMIR values, either due to the fact that large quantities of the compound were used or because the compound had a high individual MIR value.

Table 2-5: *SWA Composite Average MIRs – VOCs & Exempt Compounds Only*

Coating Category	SWA CMIR (g O₃/g product)	Primary Contributors
Antenna	2.58	Bin 14 Hydrocarbon Solvent; Bin 23 Hydrocarbon Solvent; Xylene
Bituminous Roof	0.78	Bin 14 Hydrocarbon Solvent; Bin 9 Hydrocarbon Solvent; Bin 15 Hydrocarbon Solvent
Bituminous Roof Primer	2.35	Propylene Glycol; Bin 22 Hydrocarbon Solvent; Bin 14 Hydrocarbon Solvent
Bond Breakers	5.58	Morpholine; Toluene; Hydrotreated light naphthenic distillate
Clear Brushing Lacquer	2.03	2-Butoxy Ethanol; Methyl-n-amyl Ketone; Xylene
Concrete Curing Compounds	4.67	Morpholine; Bin 22 Hydrocarbon Solvent; Bin 14 Hydrocarbon Solvent
Dry Fog	1.66	Bin 14 Hydrocarbon Solvent; Bin 9 Hydrocarbon Solvent; 2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate
Faux Finishing	2.43	Propylene Glycol; Ethylene Glycol; 2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate
Fire Resistive	2.06	Propylene Glycol, 1,2-; Ethylene Glycol; Petroleum Hydrocarbon
Fire Retardant – Clear	0.79	Aggregated VOCs < 0.1%; Formaldehyde; Isopropyl Alcohol
Fire Retardant – Opaque	2.03	Propylene Glycol; 1,2-Benzenedicarboxylic Acid, Diheptyl Ester, Branched and Linear; Xylene
Flat	2.04	1,2-Ethanediol; 2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate; Propanadiol, 1,2-
Floor	1.84	Benzyl Alcohol; Propanadiol, 1,2-; Propylene Glycol
Flow	2.87	2-Butoxyethanol; Aggregated VOCs < 0.1%
Form Release Compounds	1.08	Bin 11 Hydrocarbon Solvent; Straight-run middle distillate; Bin 15 Hydrocarbon Solvent

Table 2-5: *SWA Composite Average MIRs – VOCs & Exempt Compounds Only*

Coating Category	SWA CMIR (g O₃/g product)	Primary Contributors
Graphic Arts	2.32	Propanadiol, 1,2-; Bin 14 Hydrocarbon Solvent; Xylene
High Temperature	2.35	Bin 10 Hydrocarbon Solvent; Dimethyl Benzene; Bin 15 Hydrocarbon Solvent
Industrial Maintenance	3.07	Bin 22 Hydrocarbon Solvent; Dimethyl Benzene; Bin 6 Hydrocarbon Solvent
Lacquers	2.51	Methyl Benzene; Xylene; 2-Methyl-4-pentanone
Low Solids	2.90	Propylene Glycol; Triethylamine; 2-Butoxyethanol
Magnesite Cement	4.03	Bin 22 Hydrocarbon Solvent; 1,2,4-Trimethylbenzene; Xylene
Mastic Texture	2.48	1,2-Ethanediol; Bin 11 Hydrocarbon Solvent; Aggregated VOCs < 0.1%
Metallic Pigmented	3.51	Bin 22 Hydrocarbon Solvent; Bin 15 Hydrocarbon Solvent; Hydrotreated Heavy Naphtha
Multi-Color	2.57	Bin 22 Hydrocarbon Solvent; Triethylamine; 2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate
Nonflat - High Gloss	2.44	1,2-Ethanediol; Propanadiol, 1,2-; Diethylene Glycol Monoethyl Ether
Nonflat - Low Gloss	2.32	1,2-Ethanediol; Propanadiol, 1,2-; 2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate
Nonflat - Medium Gloss	2.29	Propanadiol, 1,2-; 1,2-Ethanediol; 2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate
Other	0.63	Hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine; Bin 15 Hydrocarbon Solvent; Xylene
Pre-Treatment Wash Primer	2.68	Ethylene Glycol; Propylene Glycol Dipropylene Glycol Butoxy Ether
Primer, Sealer, and Undercoater	2.24	1,2-Ethanediol; 2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate; Propanadiol, 1,2-

Table 2-5: *SWA Composite Average MIRs – VOCs & Exempt Compounds Only*

Coating Category	SWA CMIR (g O₃/g product)	Primary Contributors
Quick Dry Enamel	1.84	Bin 14 Hydrocarbon Solvent; Bin 6 Hydrocarbon Solvent; Bin 11 Hydrocarbon Solvent
Quick Dry Primer, Sealer, and Undercoater	2.03	Ethylene Glycol; Bin 6 Hydrocarbon Solvent; Aggregated VOCs < 0.1%
Recycled	0.91	Propylene Glycol; Texanol; Ester Alcohol
Roof	2.36	Propanadiol, 1,2-; Ethylene Alcohol; 2-Amino-2-methyl-1-propanol
Rust Preventative	2.06	Bin 22 Hydrocarbon Solvent; Bin 11 Hydrocarbon Solvent; 2-Butoxy Ethanol
Sanding Sealers	2.13	Xylene; Bin 15 Hydrocarbon Solvent; Bin 14 Hydrocarbon Solvent
Shellacs - Clear	1.68	Ethanol; Methyl Isobutyl Ketone; Isopropanol
Shellacs - Opaque	1.71	Ethanol; Aggregated VOCs < 0.1%; Isopropanol
Specialty Primer, Sealer, and Undercoater	2.81	2-(2-Butoxyethoxy)ethanol; 1,2-Ethanediol; Ethylene Glycol
Stains - Clear/Semitransparent	1.67	Bin 14 Hydrocarbon Solvent; Bin 11 Hydrocarbon Solvent; Ethylene Glycol
Stains - Opaque	2.49	1,2-Ethanediol; Stoddard Solvent; Propanadiol, 1,2-
Swimming Pool	4.13	Xylene; Bin 22 Hydrocarbon Solvent; n-Butyl Alcohol
Swimming Pool Repair and Maintenance	6.96	Xylene; 1,2,4-Trimethylbenzene; Bin 14 Hydrocarbon Solvent
Traffic Marking	0.94	Methanol; 2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate; 2-(2-Butoxyethoxy)ethanol
Varnishes - Clear	1.93	Bin 14 Hydrocarbon Solvent; Bin 15 Hydrocarbon Solvent; (2-Methoxymethylethoxy)propanol
Varnishes - Semitransparent	1.16	Bin 11 Hydrocarbon Solvent; Bin 14 Hydrocarbon Solvent; Propylene Glycol

Table 2-5: *SWA Composite Average MIRs – VOCs & Exempt Compounds Only*

Coating Category	SWA CMIR (g O₃/g product)	Primary Contributors
Waterproofing Concrete/Masonry Sealers	2.76	1,2-Ethanediol; Bin 22 Hydrocarbon Solvent; Diethylene Glycol Monomethyl Ether
Waterproofing Sealers	1.98	Bin 6 Hydrocarbon Solvent; Propanadiol, 1,2-; Bin 22 Hydrocarbon Solvent
Wood Preservatives	1.99	Aliphatic Hydrocarbons; Mineral Spirits; Bin 14 Hydrocarbon Solvent

Ozone Quantities

Ultimately, VOC emission quantities are used to determine the impact on ozone concentrations. Total VOC emissions can be converted to ozone quantities by using detailed speciation profiles, based on the results of ARB's Architectural Coating surveys. The profiles contain listings of specific chemicals, which can be associated with reactivity values for the purposes of air quality modeling. A similar exercise involves calculating the ozone generated by each ingredient in each coating product, based on the survey data, and then determining the total ozone quantity for each coating category. This can be done, using the following equations:

(1) Calculate the emissions of each VOC and exempt compound in each product:

$$[\text{TOG Emissions, tons/day}]_i = [\text{Sales, gals/yr}]*[\text{Density, lbs/gal}]*[\text{Wt\% TOG}]_i * \frac{[1 \text{ ton TOG/2000 lbs TOG}]}{[365 \text{ days/yr}]}$$

(2) Calculate the ozone generated from each VOC and exempt compound in each product:

$$[\text{Ozone, tpd}]_i = [\text{TOG Emissions, tons/day}]_i *[\text{MIR}_i, \text{g O3/g TOG}] * \frac{[907,185 \text{ g TOG/ton TOG}]}{[907,185 \text{ g O}_3/\text{ton O}_3]}$$

(3) Add up the ozone generated by all VOCs and exempt compounds in all products:

$$[\text{Total Ozone, tpd}] = [\text{Ozone, tpd}]_1 +[\text{Ozone, tpd}]_2 +\ldots+ [\text{Ozone, tpd}]_n$$

where $[\text{TOG Emissions}]_i$ = Emissions of each VOC or exempt compound "i" in a product, tons/day
Sales = Sales of each coating product, gallons/year
Density = Density of each coating product, pounds/gallon
$[\text{Wt\% TOG}]_i$ = Weight percent of each VOC or exempt compound "i" in each product
$[\text{MIR}]_i$ = the MIR of each VOC or exempt compound "i" in a product, grams ozone/grams TOG
$[\text{Ozone}]_i$ = the amount of ozone generated by each VOC or exempt compound "i", tons/day
n = the total number of VOCs and exempt compounds in all coating products

Table 2-6 contains a summary of ozone quantities, based on VOCs only. Table 2-7 contains ozone quantities for exempt compounds only, but it only includes those coating categories for which exempt compounds were reported. The survey gathered data for

more than 8,000 products. For approximately 100 products (which accounted for 2.0% of the total sales volume), no ingredient data were submitted. Therefore, it was not possible to identify individual MIRs for each ingredient in these products. As a result, the total ozone quantity provided below is slightly less than it should be, because it doesn't include the contribution from approximately 100 products that have missing ingredient data.

Table 2-6: *Ozone Quantities Based on Individual Ingredients (VOCs Only)*

Coating Category	Emissions – VOCs (tpd)	Ozone (tpd)
Antenna	0.00	0.00
Bituminous Roof	4.33	7.20
Bituminous Roof Primer	0.36	0.70
Bond Breakers	0.07	0.17
Clear Brushing Lacquer	0.53	1.08
Concrete Curing Compounds	0.37	1.58
Dry Fog	1.10	1.86
Faux Finishing	0.21	0.51
Fire Resistive	0.00	0.00
Fire Retardant – Clear	0.00	0.00
Fire Retardant – Opaque	0.02	0.06
Flat	16.28	34.84
Floor	1.48	3.72
Flow	0.00	0.00
Form Release Compounds	0.63	0.71
Graphic Arts	0.07	0.15
High Temperature	0.08	0.21
Industrial Maintenance	15.29	46.39
Lacquers	2.46	6.83
Low Solids	0.01	0.03
Magnesite Cement	0.12	0.81
Mastic Texture	0.57	0.91
Metallic Pigmented	2.89	11.22
Multi-Color	0.01	0.03
Nonflat – High Gloss	3.68	8.88
Nonflat – Low Gloss	4.01	9.36
Nonflat – Medium Gloss	15.29	34.77
Other	0.03	0.07
Pre-Treatment Wash Primer	0.10	0.23
Primer, Sealer, and Undercoater	8.38	19.11
Quick Dry Enamel	2.43	4.41
Quick Dry Primer, Sealer, and Undercoater	4.57	7.49
Recycled	0.04	0.08
Roof	0.57	1.42
Rust Preventative	0.75	1.34
Sanding Sealers	0.14	0.29

Table 2-6: *Ozone Quantities Based on Individual Ingredients (VOCs Only)*

Coating Category	Emissions – VOCs (tpd)	Ozone (tpd)
Shellacs – Clear	0.11	0.19
Shellacs – Opaque	0.51	0.88
Specialty Primer, Sealer, and Undercoater	0.31	0.78
Stains – Clear/Semitransparent	7.64	12.07
Stains – Opaque	1.40	2.94
Swimming Pool	0.06	0.26
Swimming Pool Repair and Maintenance	0.10	0.70
Traffic Marking	2.74	4.34
Varnishes – Clear	4.08	6.73
Varnishes – Semitransparent	0.30	0.33
Waterproofing Concrete/Masonry Sealers	1.29	3.69
Waterproofing Sealers	1.95	4.40
Wood Preservatives	0.65	1.19
TOTALS:	**108**	**245**

Table 2-7: *Ozone Quantities Based on Individual Ingredients (Exempt Cmpds Only)*

Coating Category	Emissions – Exempt Cmpds. (tpd)	Ozone (tpd)
Concrete Curing Compounds	0.01	0.01
Flat	0.00	0.00
Floor	0.00	0.00
High Temperature	0.01	0.00
Industrial Maintenance	0.13	0.02
Lacquers	0.37	0.16
Magnesite Cement	0.10	0.04
Metallic Pigmented	0.00	0.00
Nonflat - High Gloss	0.04	0.02
Nonflat - Low Gloss	0.00	0.00
Nonflat - Medium Gloss	0.00	0.00
Primer, Sealer, and Undercoater	0.07	0.02
Quick Dry Enamel	0.00	0.00
Quick Dry Primer, Sealer, and Undercoater	0.02	0.01
Roof	0.00	0.00
Rust Preventative	0.01	0.00
Sanding Sealers	0.00	0.00
Stains - Clear/Semitransparent	0.00	0.00
Stains – Opaque	0.00	0.00
Swimming Pool Repair and Maintenance	0.00	0.00
Traffic Marking	1.16	0.50
Varnishes – Clear	0.02	0.01

Table 2-7: *Ozone Quantities Based on Individual Ingredients (Exempt Cmpds Only)*

Coating Category	Emissions – Exempt Cmpds. (tpd)	Ozone (tpd)
Waterproofing Concrete/Masonry Sealers	0.18	0.05
Waterproofing Sealers	0.23	0.06
TOTALS:	**2.3**	**0.9**

As noted above, the ozone totals are slightly less than they should be, due to some missing ingredient data from the 2001 survey. To get an estimate of ozone quantities for the total volume of coating sales, it's possible to develop a representative reactivity value that can be multiplied by total VOC emissions to yield ozone. A representative reactivity value for this purpose would be a sales-weighted average MIR that is based on VOCs only (SWA MIR_{VOC}). This is similar to the Composite Average MIR that was previously discussed, but it would not include exempt compounds, because total VOC emissions are based on VOCs only. Using category-specific SWA MIR_{VOC} values and VOC emissions data can provide a more complete estimate of the ozone generated from coatings reported in the 2001 survey. In addition, developing SWA MIR_{VOC} values for each coating category provides a mechanism for calculating ozone from future emission inventories, based on future VOC emission data. Calculations for the SWA MIR_{VOC} values and the ozone estimates are described below:

(1) Calculate the VOC emissions for each product:

$$[\text{VOC Emissions, tons/day}] = [\text{Sales, gals/yr}]*[\text{VOC Actual, g/l}]*\frac{[1\text{ lb/gal}]}{[120\text{ g/l}]}*\frac{[1\text{ ton TOG/2000 lbs TOG}]}{[365\text{ days/yr}]}$$

(2) Calculate the total VOC emissions for each coating category:

$$[\text{Total VOC Emissions, tpd}] = [\text{VOC Emissions}]_1 +[\text{ VOC Emissions}]_2 +…+ [\text{VOC Emissions}]_n$$

(3) Determine the sales-weighted average MIR for VOCs only (SWA MIR_{VOC}), for each coating category, using the following two equations:

$$[\text{SWA }MIR_{VOC}, \text{g O}_3/\text{g TOG}] = \frac{([\text{VOC Qty}]*[\text{MIR}])_1 +([\text{VOC Qty}]*[\text{MIR}])_2 +…+ ([\text{VOC Qty}]*[\text{MIR}])_n}{[\text{Total VOC Qty}]}$$

where the quantity of VOC contained in each product is

$$[\text{VOC Qty, lbs}]_i = [\text{Sales, gals}]*[\text{Density, lb/gal}]*[\text{Wt\%VOC}]_i$$

(4) Calculate the amount of ozone generated for each coating category, based on VOC emissions and the SWA MIR_{VOC}:

$$[\text{Ozone, tpd}] = [\text{SWA }MIR_{VOC}, \text{g O}_3/\text{g TOG}]*[\text{Total VOC Emissions, tpd}] *\frac{[907,185\text{ g TOG/ton TOG}]}{[907,185\text{ g O}_3/\text{ton O}_3]}$$

where
    [VOC Emissions] = Emissions of VOCs only for each coating, tons/day
    Sales = Sales of each coating product, gallons/year
    VOC Actual = VOC Actual Content, including water and exempt compounds, grams/liter
    [VOC Qty]$_i$ = Quantity of each VOC ingredient "i" in each product, pounds
    Density = Density of each coating product, pounds/gallon
    [Wt% VOC]$_i$ = Weight percent of each VOC ingredient "i" in each product

[SWA MIR$_{VOC}$] = the sales-weighted average MIR for VOCs only, grams ozone/grams TOG
[MIR]$_i$ = the MIR of each VOC ingredient "i" in a product, grams ozone/grams TOG
[Ozone]$_i$ = the amount of ozone generated by each VOC ingredient "i", tons/day
n = the total number of VOCs in all coating products

Table 2-8 contains a summary of ozone quantities, based on total VOC emissions and a sales-weighted average MIR for VOCs only. The quantity of ozone in Table 2-8 is very close to the sum of the quantities in Tables 2-6 and 2-7, with a difference of only 1%.

Table 2-8: *Ozone Quantities Based on Total VOC Emissions*

Coating Category	VOC Emissions (tpd)	SWA MIR - VOCs only (g O₃/g TOG)	Ozone (tpd)
Antenna	0.00	2.46	0.00
Bituminous Roof	4.33	1.64	7.09
Bituminous Roof Primer	0.37	1.93	0.71
Bond Breakers	0.07	2.95	0.20
Clear Brushing Lacquer	0.53	2.03	1.07
Concrete Curing Compounds	0.37	4.71	1.75
Dry Fog	1.10	1.66	1.82
Faux Finishing	0.22	2.35	0.51
Fire Resistive	0.00	2.12	0.00
Fire Retardant – Clear	0.00	2.08	0.00
Fire Retardant – Opaque	0.02	3.59	0.06
Flat	15.60	2.14	33.32
Floor	0.87	2.64	2.30
Flow	0.00	2.88	0.00
Form Release Compounds	0.61	1.02	0.62
Graphic Arts	0.07	2.15	0.16
High Temperature	0.08	2.58	0.21
Industrial Maintenance	15.44	3.11	48.02
Lacquers	2.50	2.80	6.99
Low Solids	0.01	2.98	0.03
Magnesite Cement	0.12	7.12	0.82
Mastic Texture	0.68	1.57	1.07
Metallic Pigmented	2.81	4.25	11.95
Multi-Color	0.01	4.25	0.03
Nonflat – Low Gloss	4.05	2.34	9.49
Nonflat – Medium Gloss	15.58	2.28	35.51
Nonflat – High Gloss	3.65	2.43	8.86
Other	0.02	2.91	0.06
Pre-Treatment Wash Primer	0.10	2.35	0.23
Primer, Sealer, and Undercoater	8.55	2.28	19.50
Quick Dry Enamel	2.49	1.74	4.33
Quick Dry Primer, Sealer, and Undercoater	6.49	1.62	10.49

Table 2-8: *Ozone Quantities Based on Total VOC Emissions*

Coating Category	VOC Emissions (tpd)	SWA MIR - VOCs only (g O$_3$/g TOG)	Ozone (tpd)
Recycled	0.00	1.82	0.00
Roof	0.57	2.38	1.36
Rust Preventative	0.75	1.65	1.24
Sanding Sealers	0.14	2.11	0.29
Shellacs – Clear	0.11	1.68	0.18
Shellacs – Opaque	0.50	1.58	0.80
Specialty Primer, Sealer, and Undercoater	0.31	2.63	0.81
Stains – Clear/Semitransparent	7.86	1.49	11.70
Stains – Opaque	1.36	2.20	3.00
Swimming Pool	0.06	4.64	0.26
Swimming Pool Repair and Maintenance	0.10	7.03	0.70
Traffic Marking	3.03	1.58	4.79
Varnishes – Clear	4.03	1.62	6.51
Varnishes – Semitransparent	0.30	1.08	0.32
Waterproofing Sealers	1.92	2.39	4.59
Waterproofing Concrete/Masonry Sealers	1.30	2.87	3.73
Wood Preservatives	0.68	1.67	1.14
TOTALS:	**110**		**249**

Chapter 3 – **Future Efforts**

ARB is investigating whether a reactivity-based approach is feasible for achieving additional emission reductions from the architectural coatings category. This report represents ARB's initial efforts to document a reactivity baseline for this investigation. It is possible that implementing reactivity-based regulations will provide additional ozone benefits, while providing greater flexibility to coating manufacturers in their formulations. However, it is also possible that the investigation will determine that existing reactivity levels are already so low that the use of a reactivity-based approach would not yield significant reductions. Listed below are the primary components of ARB's continuing investigation.

Research

ARB's $300,000 architectural coating reactivity project with U.C. Riverside is ongoing and completion is scheduled for 2005. The project includes verifying the chemical mechanisms used to assess the reactivity of Texanol® and the following hydrocarbon solvents in a new state-of-the-art environmental chamber:

Table 3-1: *Hydrocarbon Solvents Being Tested in Environmental Chamber*

Hydrocarbon Solvent Name	ASTM Designation	Description	ASTM Distillation Range (ºF)	ARB Bin #
Aromatic 100	D3734, Type I	362°F maximum dry point, 95% minimum aromatic content (mostly C9's)	300-355	22
7% Aromatic Mineral Spirits	D235, Type IB	2-8% aromatics, full distillation range	300-415	14
Low Aromatic Mineral Spirits	D235, Type 1C	0-2% aromatic content, full distillation range (300-415°F)	300-415	11
Odorless Mineral Spirits	D235, Type III C-1	0-0.25% maximum aromatic, full distillation range, odorless, low olefins	300-415	12
Stoddard Solvent (15-20% Aromatic Mineral Spirits)	D235, Type 1A	8-22% aromatics, full distillation range (300-415°F)	300-415	15
V M & P Naphtha	D3735, Type IV	0-2% aromatic content, minimum flash point of 40°F	235-310	6

In 2003, SCAQMD provided $200,000 to U.C. Riverside to conduct additional reactivity research. At least four compounds will be tested in the environmental chamber, and it is likely that two of these compounds will be from water-based coatings (e.g., ethylene glycol and propylene glycol.) This project is scheduled for completion in 2004.

Both of these research projects are being coordinated with the Reactivity Research Advisory Committee (RRAC), which includes representatives from coating manufacturers, solvent manufacturers, and regulatory agencies.

2005 Architectural Coating Survey

In 2005, ARB is planning to conduct another architectural coating survey to collect sales and ingredient data for calendar year 2004. This survey would reflect the coatings being sold in California after all of the SCM VOC limits have taken effect. It is expected that results from this survey would be finalized during 2006.